

RDT&E Progress and Plans for Hexavalent Chromium (Cr⁶⁺)

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E2S2 Conference

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SERDP

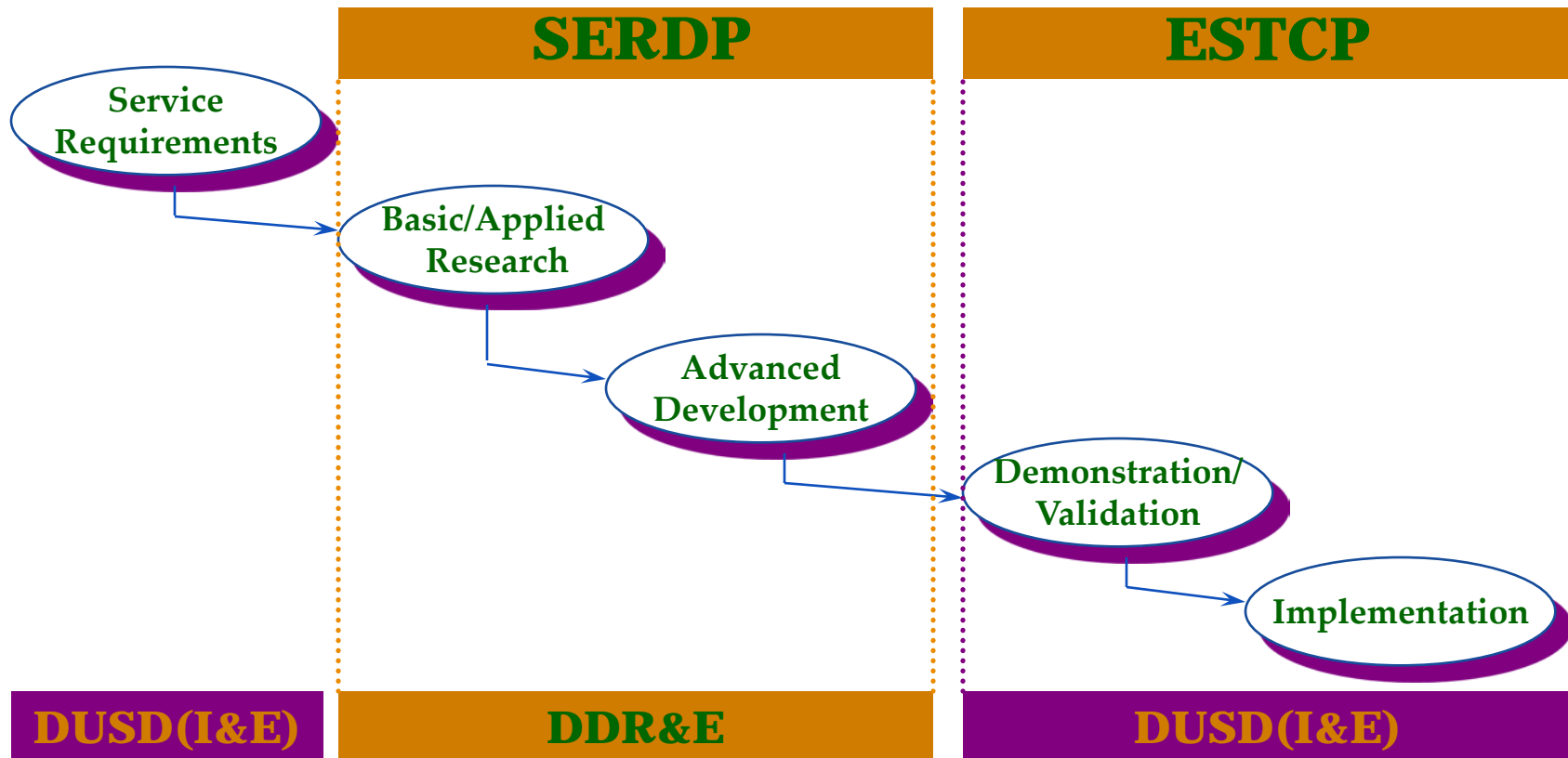
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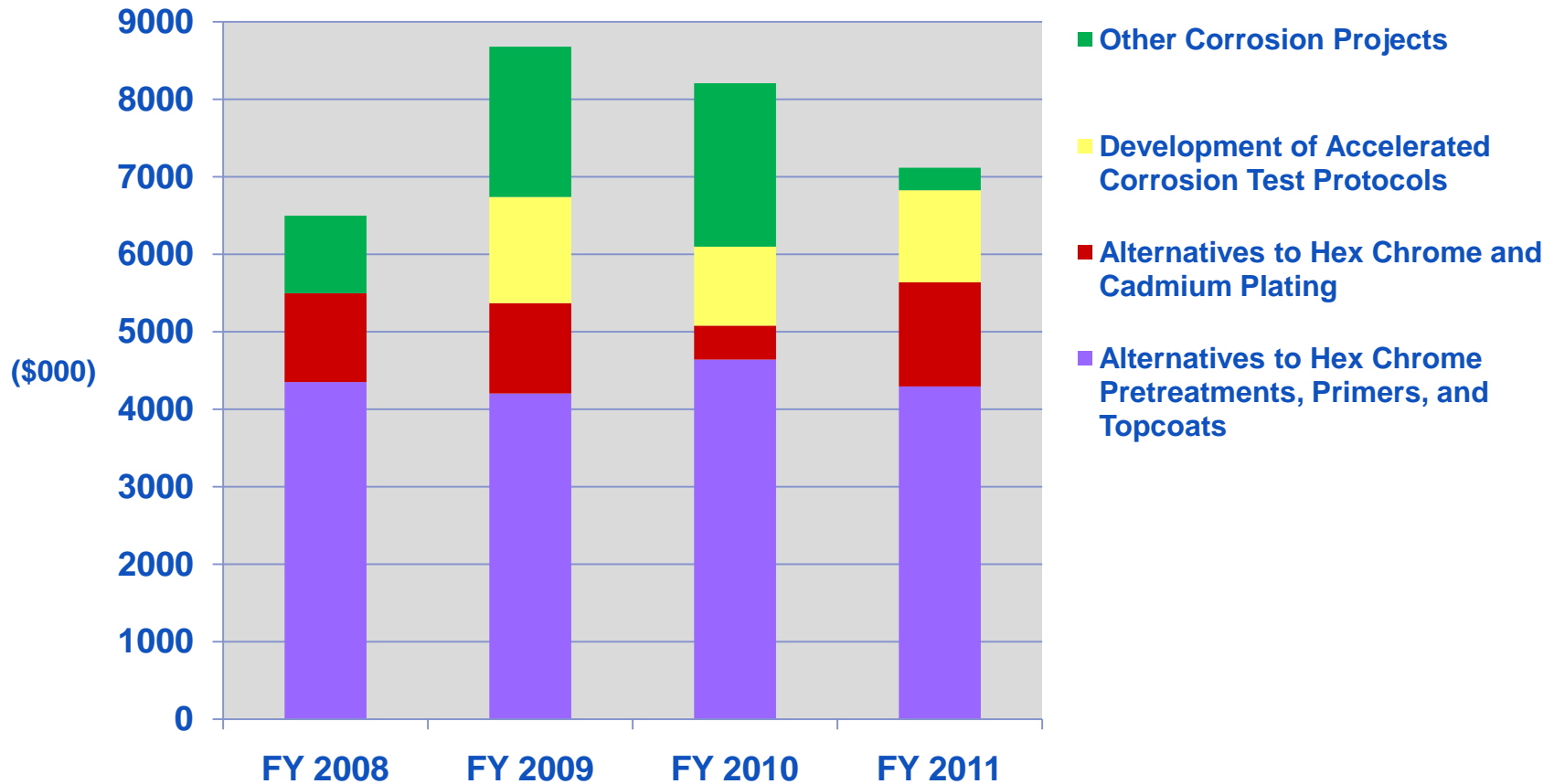
ESTCP

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Environmental Technology Development Process



SERDP/ESTCP Investments Directly or Indirectly Related to Corrosion



Total four-year investment = ~ \$ 30.2 million

Recent SERDP Cr⁶⁺-Related Projects

FY2008

- **Scientific Understanding of Non-Chromated Corrosion Inhibitors Function**
 - ◆ **WP-1618: *Corrosion Protection Mechanisms of Rare-Earth Compounds Based on Cerium and Praseodymium*** (Missouri University of Science and Technology)
 - ◆ **WP-1619: *Morphology and Mechanism of Benign Inhibitors*** (University of Cincinnati)
 - ◆ **WP-1620: *Scientific Understanding of Non-Chromated Corrosion Inhibitors Function*** (Ohio State University)
 - ◆ **WP-1621: *Scientific Understanding of the Mechanisms of Non-Chromate Corrosion Inhibitors*** (Southwest Research Institute)

Recent SERDP Cr⁶⁺-Related Projects

FY2009

- **Dynamic Accelerated Corrosion Test Protocol**
 - ◆ WP-1673: *Accelerated Dynamic Corrosion Test Method Development* (Southwest Research Institute)
 - ◆ WP-1674: *Dynamic Multivariate Accelerated Corrosion Test Protocol* (Air Force Research Lab)
- **Environmentally Acceptable, Direct-To-Substrate Pretreatments for Multi-Material Systems**
 - ◆ WP-1675: *Wash Primer Replacement Based on the Superprimer Technology* (University of Cincinnati)
 - ◆ WP-1676: *Environmentally Friendly Zirconium Oxide Pretreatment* (PPG Industries Inc.)

Recent SERDP Cr⁶⁺-Related Projects

FY2011

- Understanding Corrosion Protection Requirements for Adhesive Bond Primers
 - ♦ WP-2144: *Understanding Corrosion Protection Requirements for Adhesive Bond Primers (NAVAIR Pax River)*

Scientific Understanding of Non-Chromated Corrosion Inhibitors Function (Project WP-1620)

Project Team – Main Performers

- **Dr. Gerald S. Frankel and Dr. Rudolph G. Buchheit**
Fontana Corrosion Center, The Ohio State University
Specialists in corrosion
- **Dr. Greg Swain**
Dept of Chemistry, Michigan State University
Specialist in electrochemistry/surface analysis
- **Dr. Mark Jaworowski**
United Technologies Research Center
Specialist in surface treatments

Project Team – Advisory Group

- **Mr. Bill Nickerson, Naval Air Systems Command, Patuxent River, MD**
- **Mr. Brian Placzankis, Army Research Labs, Aberdeen Proving Ground, MD**
- **Dr. Joel Johnson, Air Force Research Labs, WPAFB**
- **Dr. Bill Fristad, Henkel Corp., Madison Heights, MI**
- **Dr. Joe Osborne, Boeing Phantom Works, Seattle, WA**

These team members are deeply involved in the development and application of chromate-free coating systems for military applications.

Technical Objective

The primary objective of this work is to develop fundamental understanding of the existing chromate-free inhibitors and inhibitory coating systems with the ultimate goals of:

- Providing scientists and engineers developing such coatings with information that will help them improve their products.**
- Providing engineers designing structures with information that will help them utilize non-chromate coating systems more effectively.**

Technical Approach

Tasks/Projects

Surface treatments and soluble inhibitors:

1. Fundamental studies of the Trivalent Chrome Process (TCP)
2. Mechanisms of selected inhibitors

Paint/pigment properties:

3. Active inhibition, barrier properties and adhesion
4. Paint adhesion strength and mechanism
5. Inhibitor activation and transport in the primer layer

System level:

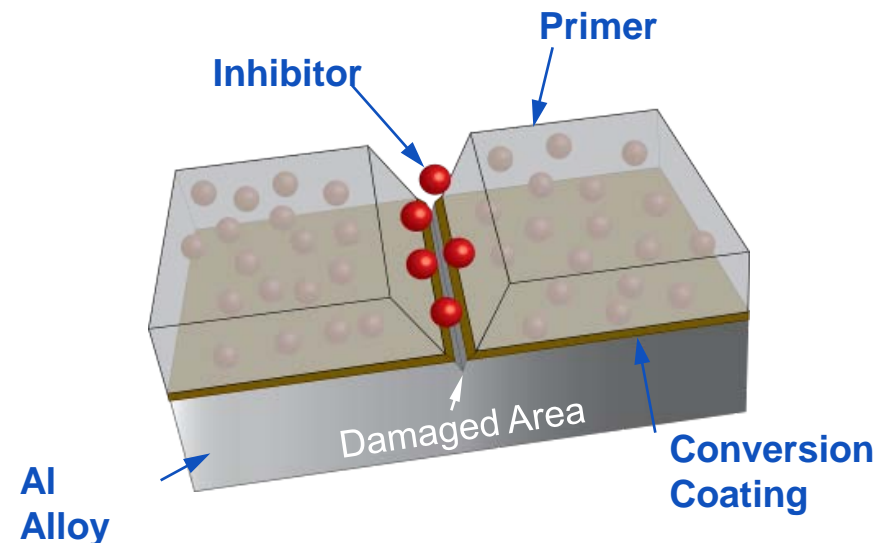
6. Interactions between polymer matrix, pigment, surface treatment, and alloy
7. Characterization of local environments in coating systems

The tasks will be performed in parallel by various team members.

Interactions between polymer matrix, pigment, surface treatment, and alloy

Background

- In chromated coating systems, chromate released from SrCrO_4 pigment dissolution in a primer layer, stabilized the artificial passivity of an underlying chromate conversion coating.
- Such a cooperative may not exist in arbitrary combinations of non-chromate passivation treatments and non-chromate primers or paints.



Questions:

- How well is the artificial passivity conferred by TCP, NCP and REM coatings reinforced by inhibitors leached from chromate-free pigments in overlying organic coatings?

Approaches:

- Interrupted exposure testing, in situ EIS and destructive forensic characterization at local defects.

Accelerated Dynamic Corrosion Test Method Development (SERDP Project WP-1673, SwRI)

- **Objective**

- ◆ Develop an improved test method to assess corrosion of new systems
 - Excite appropriate failure modes
 - Integrate representative sample designs into accelerated corrosion testing
 - Integrate mechanical loading into accelerated corrosion testing

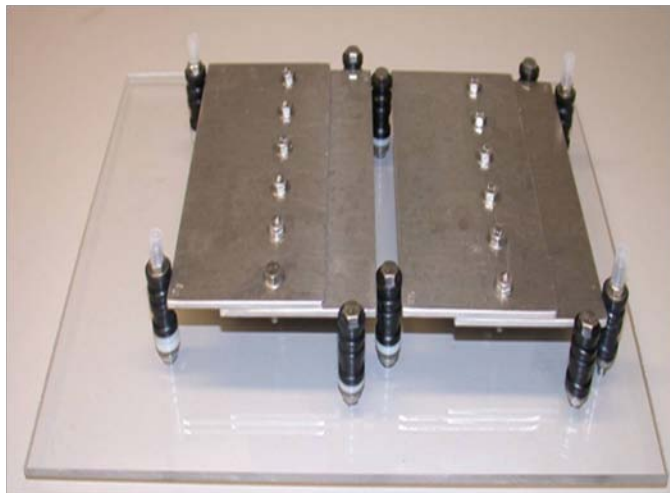
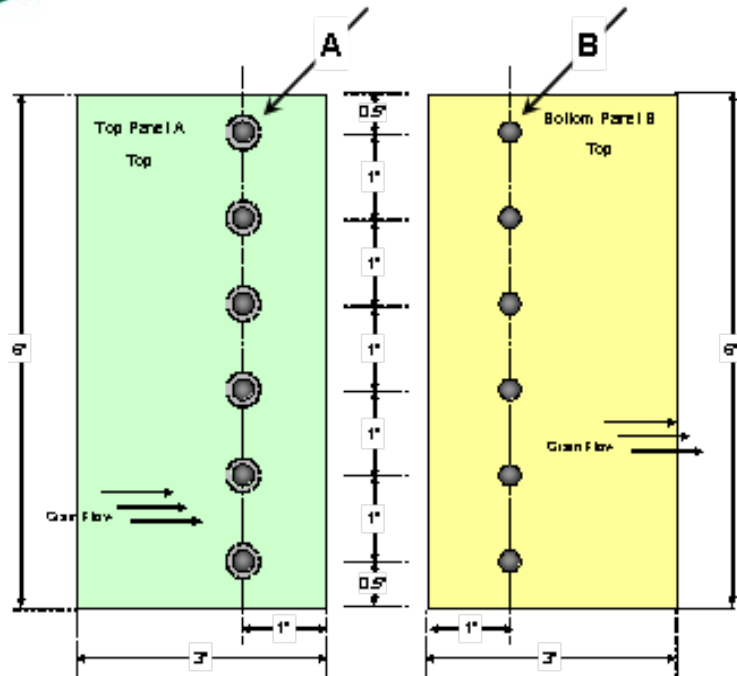
- **Approach**

- ◆ Characterize and compare the development of corrosive electrolytes for “real world” and current accelerated corrosion tests
- ◆ Determine the effect of critical environmental and mechanical parameters on degradation modes of system components
- ◆ Develop a framework to tailor the accelerated corrosion test to real world failure modes

Project Team

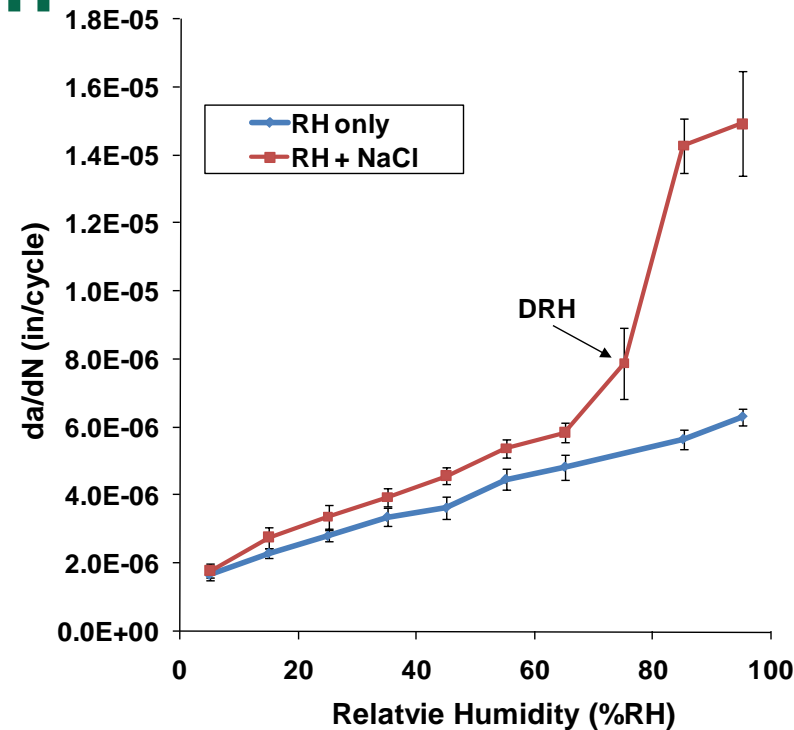
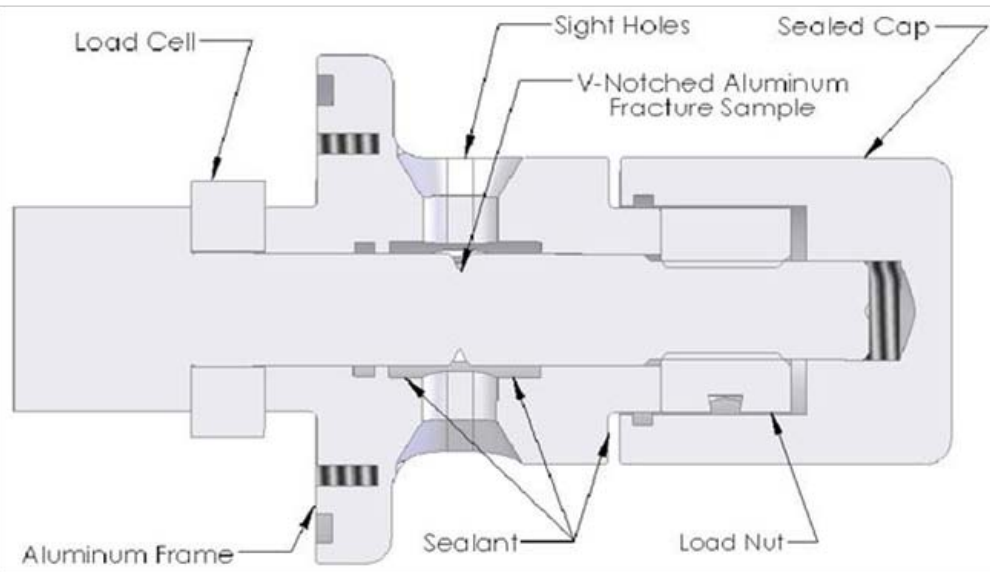
- **James Dante, Southwest Research Institute**
 - ♦ PI, electrochemistry, atmospheric corrosion, corrosion test method development
- **Craig Matzdorf, NAVAIR Pax River**
 - ♦ Co-PI, atmospheric testing, accelerated corrosion testing, qualification
- **Dr. Joseph Osborne, The Boeing Company**
 - ♦ Co-PI, coating system integration, coating and surface prep development, Cr and Cd replacement
- **Drs. Robert Kelly and Bill Keene, University of Virginia**
 - ♦ Measurement of thin film and localized electrolytes, electrochemistry, corrosion mechanisms
 - ♦ Atmospheric chemistry
- **Brian Placzankis, Army Research Lab**
 - ♦ Accelerated corrosion testing, materials qualification
- **Steve Carr, Army Aviation and Missile Command**
 - ♦ Accelerated corrosion testing, materials qualification
- **Francine Bovard, Alcoa Corporation**
 - ♦ Corrosion test method development, SAE Task Leader for accelerated aluminum corrosion test
- **Fritz Friedersdorf, Luna Innovations Inc.**
 - ♦ SCC sensors and coating properties

Sample Design

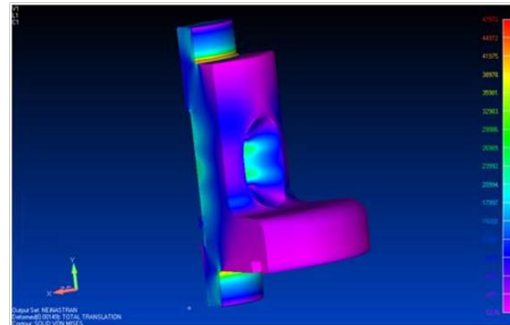


- Sample design needs to simulate:
 - ◆ Geometry with exposed and occluded areas
 - ◆ Galvanic couples between substrates and fasteners
 - ◆ Coating across discontinuities
 - ◆ Coating defects
- Sample design needs to allow for:
 - ◆ Selection of paint, fastener materials, and substrate alloys
 - ◆ External mechanical loading
- Initial design based from NAVAIR sample geometry
- Working to develop guidelines and definitions for selection and characterization of exposed panels

Effect of Environment on Cracking



- RH and NaCl effect SCC behavior
- SCC sensor being modified for measuring SCC in outdoor or laboratory environments



Selected ESTCP Projects Related to Cr⁶⁺

- **FY2000: *Non-chromate Aluminum Pre-treatments (NAVAIR Pax River)***
- **FY2003: *Development of Ferrium S53 High-Strength, Corrosion-Resistant Steel, (Hill AFB)***
- **FY2005: *Validation of Novel Electroactive Polymers as Environmentally Compliant Coatings for Replacement of Hexavalent Chromium Pretreatments (NAVAIR China Lake)***
- **FY2006: *Supersonic Particle Deposition for Repair of Magnesium Components (Army Research Lab)***
- **FY2006: *Low Temperature Powder Coatings (Hill AFB)***
- **FY2008: *Ultraviolet Curable Powder Coatings (AFRL)***
- **FY2008: *Ultraviolet Curable Coatings for Aerospace Applications (Hill AFB)***
- **FY2009: *Validation/Demonstration of Anti-Corrosion Inhibitor Primer Formulations as Replacements for Hexavalent Chromium Military Primer Coatings (NAVAIR China Lake)***

Selected ESTCP Projects Related to Cr⁶⁺

- ***FY2009: Non-Chromate, ZVOC Coatings for Steel Substrates on Army and Navy Aircraft and Ground Vehicles (ARL)***
- ***FY2009: Electrodeposition of Nanocrystalline Co-P Coatings as a Hard Chrome Plating Alternative (NAVAIR Jacksonville)***
- ***FY2010: Electrocoat Process for Non-Chromate Primers in DoD Manufacturing (NAVAIR Pax River)***
- ***FY2011: Chromium Elimination and Cannon Life Extension (Benet Weapons Lab)***
- ***FY2011: Comprehensive Evaluation and Transition of Non-Chromated Paint Primers (NAVAIR Pax River)***

Development of S53 Ultra-High-Strength (UHS) Corrosion-Resistant Stainless Steel

- Ultimate objective was to develop UHS stainless steel to replace UHS low-alloy steels such as 4340 that require cadmium plating and Cr^{6+} post treatment for corrosion protection
- Started as SERDP Exploratory Development (SEED) project in December 1999; SERDP full project started in June 2001
- Transitioned to ESTCP project in March 2003
- Developed under Accelerated Insertion of Materials (AIM) program
- First military component (A10 drag brace) fabricated in December 2005

Demonstration Tests at Hill AFB

A-10 Main Landing Gear Piston

- Performed landing gear strut testing of S53 Main Landing Gear Piston to qualification standards per Mil-A-8866 - **Successfully Completed 4 Lifetime Test**
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - **Awaiting Approval**

A-10 Nose Landing Gear Drag Brace

- Perform landing gear strut testing of S53 Main Landing Gear Drag Brace Strut to qualification standards per Mil-A-8866 - **Complete**
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - **Awaiting Potential Approval**

A-10 Nose Landing Gear Axle

- Analysis and Design to Achieve Final Qualification - **Complete**
- Conduct a Field Service Evaluation with fully processed components on an A-10 aircraft - **Awaiting Potential Approval**

T-38 Piston

- Performed landing gear strut testing of S53 Main Landing Gear Piston to qualification standards per Mil-A-8866 - **Successfully Completed 5 Lifetime Test**
- Conduct a Field Service Evaluation with fully processed components on a T-38 aircraft - **December 2010**

A10 Demonstration Components



A-10 main landing gear piston (4330V – 240 ksi)
More complex loading
Forged component



A-10 drag brace (300M - 270 ksi)
Simple tension loading
No forging required
Corrosion related failures



A-10 nose
landing
gear axle

Examples of *Ferrium* S53[®] Market Adoption

Application Examples

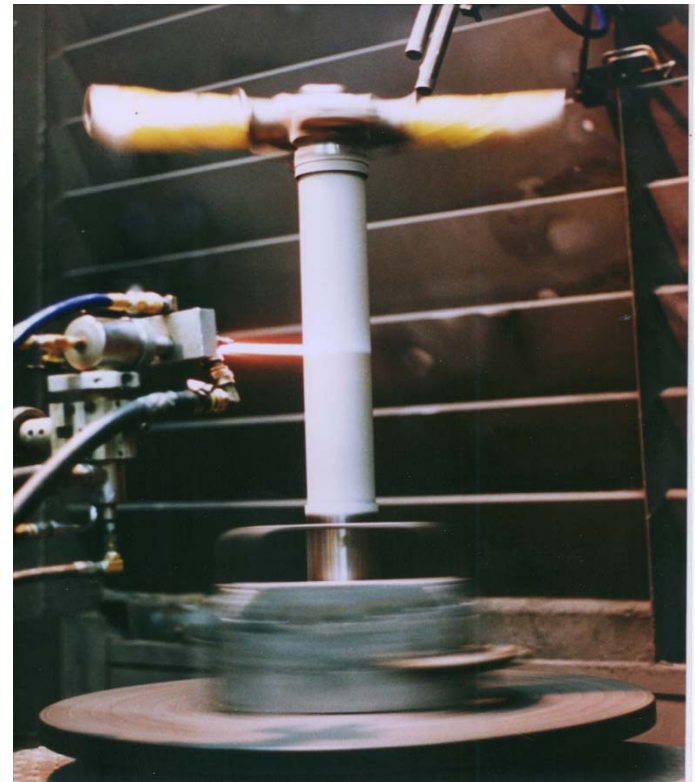
- Aircraft landing gear - parts in production and preparing for flight by USAF; commercial landing gear parts in detailed evaluation
- Auxiliary aircraft equipment - parts specified for use in major next-generation commercial aircraft platform aux equipment
- Motion control devices - parts specified for aerospace platforms
- Drive shafts - demonstration helicopter rotor driveshafts in progress
- Extensive market qualifications/property data resources -
 - ◆ CINDAS ASMD data base
 - ◆ MMPDS-04 CN1
 - ◆ SAE AMS 5922
- Robust supply chain -
 - 2 competing licensees:



Qualification of HVOF Coatings on Different Types of Aircraft Components

- Separate ESTCP projects were executed for EHC replacement related to:
 - ◆ Landing Gear
 - ◆ Propeller Hub Components
 - ◆ Hydraulic Actuators
 - ◆ Gas Turbine Engine Components
 - ◆ Helicopter Dynamic Components (rotor heads, transmissions, gearboxes, etc.)
- Projects ran from 1996-2006

HVOF Thermal Spraying of WC/17Co onto nose landing gear cylinder



HVOF Implementation - Military aircraft

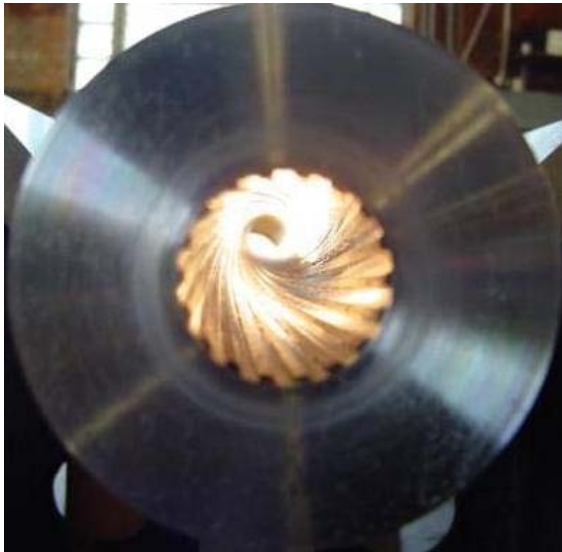
- **Joint Strike Fighter (F-35) landing gear – all variants**
- **Hill Air Force Base (Ogden Air Logistics Center) putting HVOF into production on hundreds of landing gear components on various types of aircraft; requiring vendors to provide HVOF on landing gear, not hard chrome**
- **Boeing X-45C UCAV has some HVOF WC-CoCr coated landing gear components**
- **F-18 steering covers and shock absorber piston heads with Tribaloy 400**
- **CH-53 blade damper internal-surface coatings of Tribaloy 400 have been approved**
- **C-17 nose landing gear post: HVOF WC-Co has replaced hard chrome to prevent heat-burning**
- **F-22 convergent nozzle actuators: shafts coated with WC-Co, internal surfaces coated with Tribaloy 400 alloy.**

HVOF Implementation – Commercial Aircraft

- All new Canadian landing gear designs specified with HVOF WC-CoCr
 - ◆ 4 HVOF shops set up to meet demand
- In commercial use for
 - ◆ Boeing 767-400
 - ◆ Boeing 787
 - ◆ Airbus A380
- Maintenance, Repair and Overhaul
 - ◆ Boeing has approved for thickness $< 0.015''$
 - ◆ Delta now using for maintenance
 - ◆ HVOF now used for repair of flap tracks

Eliminating Chromium from Medium Caliber Gun Barrels

Team: Benet Laboratories, Army Research Laboratory, Ares Inc., High Energy Metals, Inc., TPL, Inc., General Dynamics ATP



Results

- Process to explosively bond Tantalum-10% tungsten liners to the insides of medium caliber cannons.
- Firing tests demonstrated that the lined tube showed superior wear resistance – lasts twice as long as chrome-plated tube.



Benefits

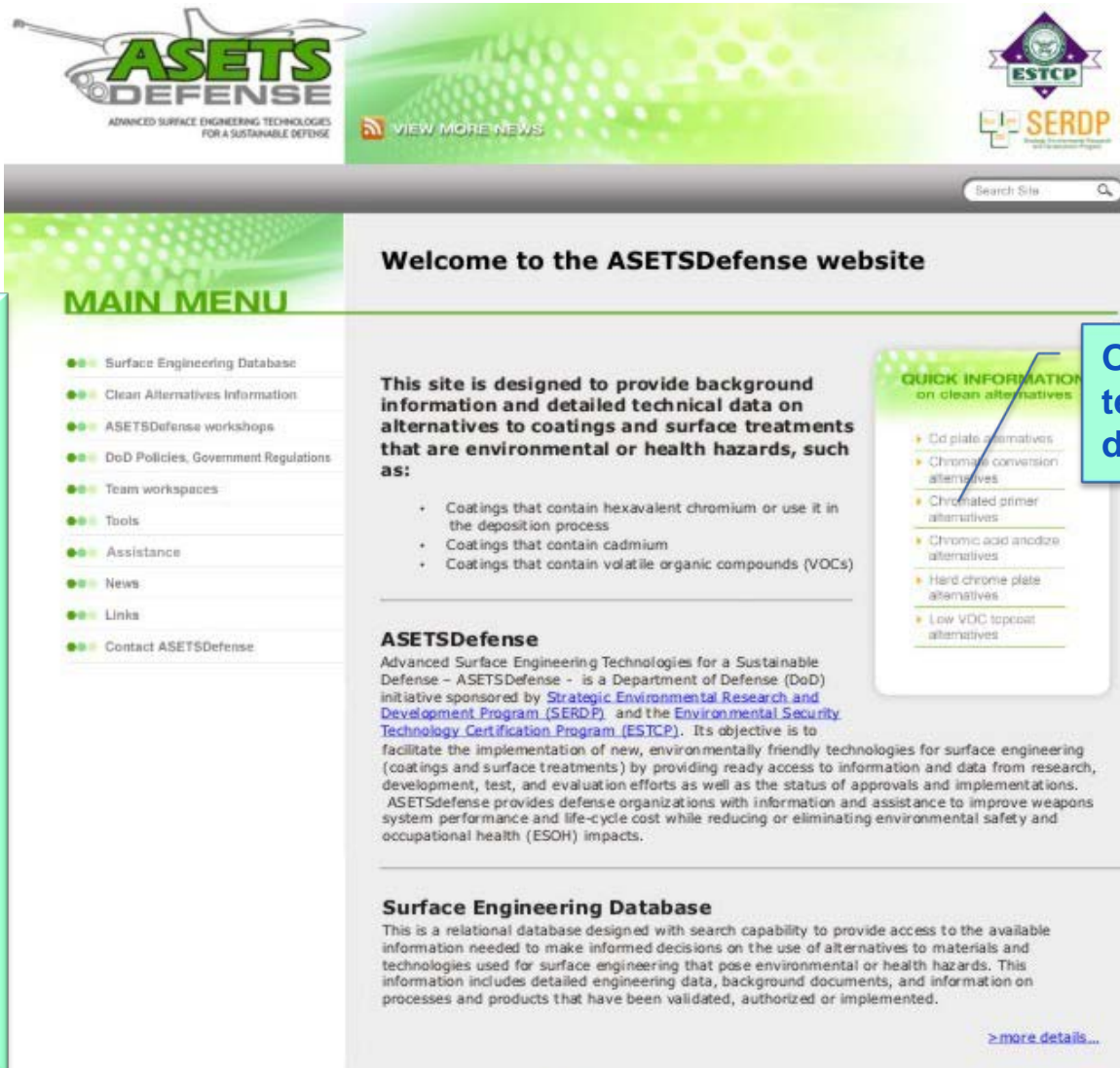
- Eliminates the use of hexavalent chromium in medium caliber gun barrels while providing superior performance and reduced life cycle costs.

SERDP/ESTCP Initiative



- Numerous surface-engineering-related projects executed by SERDP, ESTCP and other organizations to develop and evaluate new technologies that are more environmentally friendly and reduce life-cycle costs
- Problem is that stakeholders and weapons systems owners do not have ready access to data to determine if new technology can be implemented
- ASETSDefense is initiative intended to develop information data bases and organize workshops associated with technologies in the surface engineering field; web site www.asetdefense.org is entry point to engineering data and materials selection data bases under development

www.asetdefense.org



The screenshot shows the ASETDefense website homepage. At the top, there is a header with the ASETDefense logo (Advanced Surface Engineering Technologies for a Sustainable Defense) and a 'VIEW MORE NEWS' button. To the right of the header are logos for ESTCP and SERDP. Below the header is a search bar. The main content area is divided into two columns. The left column contains a 'MAIN MENU' with links to: Surface Engineering Database, Clean Alternatives Information, ASETDefense workshops, DoD Policies, Government Regulations, Team workspaces, Tools, Assistance, News, Links, and Contact ASETDefense. The right column features a 'Welcome to the ASETDefense website' message, followed by a section titled 'This site is designed to provide background information and detailed technical data on alternatives to coatings and surface treatments that are environmental or health hazards, such as:' with a bulleted list of hazards: Coatings that contain hexavalent chromium or use it in the deposition process, Coatings that contain cadmium, and Coatings that contain volatile organic compounds (VOCs). Below this is a section for 'ASETDefense' describing its mission and objectives. At the bottom of the right column is a section for the 'Surface Engineering Database' with a link to '> more details...'. A 'QUICK INFORMATION on clean alternatives' box is also visible on the right side of the main content area.

Menu

- Surface Engineering Database
- Clean Alternatives Information
- ASETDefense Workshops
- DoD Policies, Government Regulations
- Team Workspaces
- Tools
- Assistance
- Links
- Contact ASETDefense

Submenus drop down on click

One-page technology descriptions

ASETSDefense Workshop

- Held 7-10 February 2011 in New Orleans, LA
- 241 attendees representing DoD labs and repair facilities, OEMs, and vendors
- Covered all ESOH coating and surface finishing issues in new and legacy aircraft, vehicles and ships
- Focus was on Cr⁶⁺ as a result of USD (AT&L) memo
- 51 presentations covered research & development, demonstrations and implementations of alternative technologies
- Held side meeting on *Computational and Data Base Methods for Design and Prediction*
- Workshop summary plus all presentations are available on web site, www.asetdefense.org
- Next workshop planned for August 2012

Information Resource

For additional information on all SERDP and ESTCP projects, visit the new SERDP-ESTCP web site:

www.serdp-estcp.org